

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

BD

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :	A1	(11) International Publication Number: WO 90/07546
C08J 9/04, 9/12, 9/14		(43) International Publication Date: 12 July 1990 (12.07.90)

(21) International Application Number: PCT/US89/05866	(81) Designated States: BR, HU, NO.
(22) International Filing Date: 22 December 1989 (22.12.89)	Published <i>With international search report</i>
(30) Priority data: 292,036 30 December 1988 (30.12.88) US	
(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).	
(72) Inventors: CHUM, Steve, Pak-Wing ; 126 Juniper Street, Lake Jackson, TX 77566 (US). RUBENS, Louis, C. ; 503 Linwood Drive, Midland, MI 48640 (US).	
(74) Agent: MACLEOD, Roderick, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).	

(54) Title: CLOSED CELL MICROCELLULAR FOAMS AND THEIR METHOD OF MANUFACTURE

## (57) Abstract

Closed cell microcellular foam having cells with diameters of less than 10  $\mu\text{m}$  and preferably having a density is less than 0.1 gm/cm<sup>3</sup> are prepared from copolymers of  $\alpha$ -olefin and  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid. The copolymer is permeated with a blowing agent and ammonia at a pressure of 1.4 to 20 mPag in the presence of an inert gas and subsequently is heated by electromagnetic radiation of 0.1 to 200 MHz.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LJ	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

CLOSED CELL MICROCELLULAR  
FOAMS AND THEIR METHOD OF MANUFACTURE

The invention relates generally to the field of closed cell microcellular foams and specifically to closed cell microcellular foam sheet. The invention also relates to a method for preparing microcellular foams having closed cells with diameters of less than 10 micrometers ( $\mu\text{m}$ ).

A polymeric foam is commonly classified as microcellular if it has cells having diameters on the order of 30  $\mu\text{m}$  or less. However, for the purposes of this application, a microcellular foam has closed cells with diameters on the order of 10  $\mu\text{m}$  or less.

A major application of microcellular foam technology is in packaging of foods, chemicals and consumer products. Microcellular foams exhibit higher impact resistance at smaller cross-sectional areas when compared with larger celled foam.

Medical uses for microcellular foam have been identified. These uses include artificial skin and blood vessels. Small cell size and resultant high surface area per millimeter (mm) of thickness also make microcellular foam compositions of potential interest as

filters, ion exchange supports, low dielectric insulation materials, filter chromatography substrates and catalytic substrates.

5 Early processes for producing microcellular foam were developed at the Massachusetts Institute of Technology in the 1980's. Batch and extrusion processes for preparation of closed cell microcellular foam having cells with a diameter of less than 10 microns ( $\mu\text{m}$ ) are disclosed in Martini-Vvedensky, et al., U.S. Patent No. 10 4,473,665. Supersaturation of the plastic with gases permits one to control the number of cell nucleation centers.

15 Rubens, U.S. Patent No. 3,711,430 discloses closed cell microcellular foam and Q method of preparation which utilizes radio frequency (RF) radiation to foam a copolymer permeated with a combination of a perchlorofluorocarbon and ammonia. The foam has a cell size which is reduced by a factor of 10-20.

20 Using the method of Rubens, the present inventors are not able to prepare a foam with cell size of less than from about 30 to about 100  $\mu\text{m}$  in diameter.

25 Pollard, et al., U.S. Patent No. 3,013,996 discloses a method of subjecting expandable styrene polymer particles containing a volatile organic fluid to heat in a pressurized nitrogen gas ( $\text{N}_2$ ) and/or air environment. The pressure is from 200 to 2000 pounds per square inch gauge (1.4 - 14 mPag) and the temperatures range is between 50°C and 85°C for a time of from 0.5 to 72 hours sufficient to allow the gas to diffuse substantially throughout the polymer particles.

The pressure is then released to atmospheric pressure in order to foam the particles which are then quickly treated with hot water for a time of not more than 30 seconds and subsequently treated with cold water.

5 Other existing methods for preparing microcellular foams include techniques such as classical phase inversion, sintering, and nuclear bombardment. In general, these processes produce foams with density greater than 0.1 gram per cubic centimeter ( $\text{g}/\text{cm}^3$ ) (6.4 pounds per cubic foot ( $\text{lb}/\text{ft}^3$ )).

10 It would be desirable to be able to prepare a microcellular foam having cells with a diameter of less than 10  $\mu\text{m}$ .

15 It would also be desirable to be able to prepare a microcellular foam having cells with a diameter of less than 10  $\mu\text{m}$  and also having a density of less than 0.1  $\text{g}/\text{cm}^3$  (6.4  $\text{lb}/\text{ft}^3$ )

20 A first aspect of the invention is a method for preparing a closed cell microcellular foam comprising the steps of: (a) permeating a copolymer of at least one  $\alpha$ -olefin and at least one  $\alpha,\beta$ -mono-ethylenically unsaturated carboxylic acid, by pressurizing using an inert gas in the presence of a blowing agent and ammonia for an incubation time sufficient to effect a substantial diffusion of the inert gas, the blowing agent and the ammonia throughout the copolymer, the pressurizing being sufficient to maintain a pressure from about 1.4 mPag (200 psig) to about 20 mPag (3,000 psig); and thereafter (b) heating the permeated copolymer in a field of electromagnetic radiation of from about 0.1 megahertz (MHz) to about 200 MHz to

prepare a closed cell microcellular foam wherein the foam contains cells with a diameter of less than 10  $\mu\text{m}$ .

A second aspect of the invention is a closed cell microcellular foam comprising a copolymer of at least one  $\alpha$ -olefin and at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid wherein the foam has cells having diameters of less than 10  $\mu\text{m}$ .

In a typical method for preparing the microcellular foam of the present invention, an olefinic copolymer having carboxylic acid moieties is placed in an enclosed space and cooled to a temperature of from about -175°C (degrees centigrade) to about 0°C, preferably from about -80°C to about 0°C. Ammonia and at least one blowing agent are introduced as liquids into the enclosed space in an amount needed to submerge the copolymer and react with at least 85 percent of the carboxylic acid moieties of the copolymer. The enclosed space is then pressurized using an inert gas to a pressure of from about 200 pounds per square inch gauge (psig) (1.4 mPag) to about 1000 psig (7 mPag), preferably from about 200 psig (1.4 mPag) to about 800 psig (5.5 mPag). The enclosed space is heated slowly to a temperature of greater than 60°C but no greater than 1° below the melt temperature of the copolymer, preferably around 72°C. The copolymer is maintained at that temperature and pressure in an inert gas environment for an incubation time that is equivalent to at least 1/2 hour (h). Preferably the incubation time ranges from about 1/2 h per mm of thickness of the copolymer to about 12 h per mm thickness. More preferably, the incubation time ranges from about 1/2 h to about 4 h per mm of thickness of the copolymer.

5        The pressure rises autogeneously above the prepressurized pressure as the temperature rises in the enclosed space. Preferably the final pressure range is from about 300 psig (2 mPag) to about 3000 psig (20 mPag), more preferably from about 300 psig (2 mPag) to about 800 psig (5.5 mPag).

10      The permeated copolymer is cooled, usually to a temperature of about -100°C to about 10°C and removed from the enclosed space. The permeated copolymer is then heated in a dielectric heating means such as a 15,000 to 10,000 watt radiowave frequency (RF) oven to prepare a microcellular foam. The RF oven emits electromagnetic wave radiation at a frequency from about 10 MHz to about 100 MHz, preferably from about 6 MHz to about 100 MHz. The frequency may reach 200 MHz.

20      Blowing agents which can be used in the present invention method include but are not limited to halogenated C<sub>1</sub>-C<sub>6</sub>, preferably C<sub>1</sub>-C<sub>4</sub> alkyls, C<sub>1</sub>-C<sub>6</sub>, preferably C<sub>1</sub>-C<sub>4</sub> alkyls, chlorofluorohydrocarbons, chlorofluorocarbons, fluorocarbons, fluorohydrocarbons and carbon dioxide (CO<sub>2</sub>). Preferably, a blowing agent is selected from the group consisting of chlorofluoro-25 carbons and chlorofluorohydrocarbons, such as 1-chloro-1,1-difluoroethane. More preferably the blowing agent is 1,1,2,2-tetrafluro-1,2-dichloroethane (CFC 114).

30      The inert gas usually is selected from the group consisting of nitrogen, helium, neon, argon, krypton, xenon, radon and mixtures thereof. Typically the gas phase in the enclosed space is substantially the inert gas, preferably nitrogen, however the gas phase also contains trace amounts of chlorofluorocarbon,

ammonia, oxygen, water vapor, carbon dioxide and the like. The vaporized chlorofluorocarbon and ammonia are in equilibrium with a liquid phase of these compounds which completely cover the copolymer. Trace amounts of air can enter the system and contribute oxygen and carbon dioxide elements to the enclosed space.

Olefin/carboxylic acid copolymers contemplated for use in the present invention method include both random copolymers and graft copolymers. These copolymers can be obtained commercially or they can be prepared by a variety of suitable techniques well known in the polymerization art. While the invention is not to be limited to or bound by any particular technique for preparing the copolymers, suitable methods for preparing graft copolymers which can be used in the practice of this invention are disclosed in Nowak, et al., U.S. Patents 3,177,269 and Nowak, U.S. Patent No. 3,270,090, the teachings of which are herein incorporated by reference.

In either the random or the graft copolymers suitable for use in the practice of this invention, it is generally preferred that the copolymer contain between about 70 and about 95 weight percent of combined olefin and between about 5 and about 30 weight percent of combined carboxylic acid, the weight percent being based on the weight of the copolymer.

Usually  $\alpha$ -olefins having from about 2 to about 8 carbons per molecule, preferably from about 3 to about 8 carbons, can be employed in preparing the copolymers. Exemplary olefins within this class include ethylene, propylene, 1-butene, 1-pentene, 2-pentene, 1-hexene, 3-hexene, 3-methyl-1-butene, 4-methyl-1-pentene, 4-methyl-

1-hexene, styrene, and the like. Copolymers employing ethylene or propylene as the olefin are generally preferred.

Any  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid having from about 2 to about 8 carbons per molecule, preferably from about 3 to about 8 carbons, which is copolymerizable with an olefin of the class described above or which is suitable for grafting onto a homopolymer of an olefin of the class described above, can be used to prepare a copolymer for use in the present invention. Exemplary acids within this class include monocarboxylic acids and polycarboxylic acids selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, isocrotonic acid, tiglic acid, angelic acid, senecioic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid and combinations thereof. Among these, acrylic acid is preferred. The preferred copolymer is poly(ethylene/acrylic acid).

The term used to describe the acid portion of the copolymer of this invention is intended to include suitable  $\alpha,\beta$ -monoethylenically unsaturated anhydrides of carboxylic acids such as maleic anhydride. Although maleic anhydride is not a carboxylic acid because it does not have a hydrogen attached to the carboxylic groups, it is considered to be an acid for the purpose of this invention because its chemical reactivity is that of an acid.

The copolymer need not necessarily comprise a two-component copolymer. Thus, although the olefin content of the copolymer desirably should be at least 70 weight percent by weight of the copolymer, more than one

olefin can be employed. Additionally any third copolymerizable monomer can be employed in combination with the olefin and the carboxylic acid comonomers. The ionic hydrocarbon copolymers described in Rees, U.S. Patent 3,264,272 may also be used in the present invention.

A foam of the present invention usually has a density of from about  $0.01\text{ g/cm}^3$  ( $0.64\text{ lb/ft}^3$ ) to about  $0.5\text{ g/cm}^3$  ( $32\text{ lb/ft}^3$ ), preferably from about  $0.01\text{ g/cm}^3$  ( $0.64\text{ lb/ft}^3$ ) to about  $0.1\text{ g/cm}^3$  ( $6.4\text{ lb/ft}^3$ ). The cell diameter can range from about  $1\text{ }\mu\text{m}$  to about  $10\text{ }\mu\text{m}$ , preferably from about  $2\text{ }\mu\text{m}$  to about  $9\text{ }\mu\text{m}$ , especially from about 2 to about 5.

The carboxylic acid portion of the copolymer may be complexed with a metal cation. If a metal ion is complexed with the carboxylic acid moieties of the copolymer to form a metal salt of the copolymer, the resulting copolymer is referred to as an ionomer. The metal ion comprises the cationic form of a metal selected from the group consisting of alkali metal, especially alkaline earth metal, transition metal and combinations thereof. Preferably, the metal ion is the cation form of a metal selected from the group consisting of lead, gold, bismuth, copper, silver, sodium, magnesium, silicon, strontium, platinum and combinations thereof. More preferably, the metal cation is selected from the group consisting of magnesium and lead. Usually at least 15 percent of the carboxylic acid is complexed with cation in said ionomers.

The ionomer can be crosslinked before the permeation step in the enclosed space. Crosslinking is usually required when the ionomer is formed from a metal

salt where the metal is selected from lead, bismuth, silver, copper and combinations thereof. One method of crosslinking is to expose this copolymer to electron bombardment such as with a beam of about one to about four million electron volts (Mev) for a time sufficient 5 to deliver a dosage of about 5 to about 30 megarads.

In a preferred embodiment an olefin copolymer comprising from about 70 weight percent to about 95 weight percent by weight of the copolymer of an α-olefin 10 having from about 2 to about 8 carbons, preferably from about 3 to about 8 carbons, and from about 5 weight percent to about 30 weight percent by weight of the copolymer of an α,β-monoethylenically unsaturated carboxylic acid having from about 2 to about 8 carbons, 15 preferably about 3 to about 8 carbons, is combined with a metal cation to form an ionomer. The mass is compression molded to form a sheet. The sheet is permeated with a chlorofluorocarbon blowing agent and 20 ammonia in an inert gas environment at high pressure. The sheet is then foamed in a 5000 to about a 10,000 watt RF oven for about one minute at a frequency from about 0.1 MHz to about 1 MHz. Preferably, the 25 microcellular foam sheet has a thickness of less than 1/2 inch (13 mm).

The following examples are illustrative of preferred embodiments of the present invention.

30 Example I - Preparation of an Ionomeric Microcellular Foam Sheet

A compression molded ionomer sheet (2 in x 2 in x 0.12 in) (50 mm x 50 mm x 3 mm) is made by reacting a copolymer of ethylene/acrylic acid (20 weight percent acrylic acid based on the weight of the copolymer) and a

sufficient amount of magnesium oxide to complex magnesium with about 15 percent of the acrylic acid groups along the copolymeric backbone. The sheet is placed into a 600 cm<sup>3</sup> pressure reactor equipped with a mechanical stirrer. The reactor is cooled in dry ice to -78°C, and 190 cm<sup>3</sup> of liquid blowing agent, such as 5 1,1,2,2-tetrafluoro-1,2-dichloroethane (CFC 114), and 10 cm<sup>3</sup> of liquid ammonia are introduced into the reactor, 10 submerging the ionomer sheet. The pressure reactor is pressurized with N<sub>2</sub> to a pressure of 200 psig (1.4 mPag).

The reactor is heated using a heating mantle to a temperature of about 75°C +/- 1°C. Concurrently, the 15 liquid blowing agent/ammonia mixture in the reactor is stirred mechanically at 100 rpm. After 72 hours, the reactor is cooled in dry ice to a temperature of -78°C. The liquids are removed and the gas pressure is released. The reactor is opened and the sheet which is 20 impregnated with CFC 114, ammonia and nitrogen gas (N<sub>2</sub>) is removed and immediately heated in a 5000 watt RF oven at 6 MHz for about 1 minute. The resultant micro-cellular foam sheet contains cells having a diameter of 25 about 7 µm and a density of about 0.05 g/cm<sup>3</sup> (3.2 lb/ft<sup>3</sup>).

Example II - Preparation of Ionomeric Microcellular Foam Sheet

The procedure described in Example I is 30 followed. A compression molded ionomer sheet (2 in x 2 in x 0.04 in) (50 mm x 50 mm x 1 mm) is made from the copolymer of ethylene/acrylic acid and magnesium oxide, as in Example I, and placed in a 600 cm<sup>3</sup> reactor. The reactor is cooled to a temperature of -78°C and 190 cm<sup>3</sup> of liquid CFC 114 and 10 cm<sup>3</sup> of liquid ammonia are

introduced into the reactor, submerging the sheet. The reactor is pressurized with N<sub>2</sub> to a pressure of about 400 psig (2.8 mPag). The reactor is heated to 75°C and the sheet is incubated in N<sub>2</sub>, ammonia and CFC 114 for 25 hours. The reactor is cooled and the liquids and gases are removed. The sheet which is impregnated with CFC 114, ammonia and N<sub>2</sub> is removed and immediately heated in a 5000 watt RF oven at 6 MHz for about 1 minute. The resulting microcellular foam sheet has a density of about 0.05 g/cm<sup>3</sup> (3.2 lb/ft<sup>3</sup>) and an average cell diameter of approximately 5 μm.

Example III - Preparation of Ionomeric Microcellular Foam Sheet

The procedure described in Example I is followed. A compression molded ionomer sheet (2 in x 2 in x 0.05 in) (50 mm x 50 mm x 1.25 mm) consisting of a copolymer of ethylene/acrylic acid and lead (20 weight percent of acrylic acid based on the total weight of the copolymer and 15 weight percent of lead based on the weight of acrylic acid) is crosslinked by exposure to a 2 Mev electron beam for a time sufficient to deliver a dosage of 15 megarads. The sheet is placed in a reactor and cooled to about -78°C and 190 ml of liquid CFC 114 and 10 ml of liquid ammonia are introduced into the reactor, submerging the sheet. The reactor is pressurized to about 200 psig (1.4 mPag) with N<sub>2</sub>. The temperature is raised to 75°C and the sheet is exposed to the resulting N<sub>2</sub>, CFC 114, and ammonia environment for 48 hours. The reactor is cooled to -78°C and the liquids and gases are removed. The sheet, impregnated with N<sub>2</sub>, ammonia and CFC 114, is removed to a 10,000 watt RF oven and heated at 10 MHz for about one minute. The resulting microcellular foam sheet has a density of

-12-

about  $0.05 \text{ g/cm}^3$  ( $3.2 \text{ lb/ft}^3$ ) and has cells with an average diameter of about  $8 \mu\text{m}$ .

Cell diameters are measured from scanning electron micrographs taken at random cross-section intervals in the microcellular foam sheets. Foam density is measured using standard ASTM testing method, D-1622-83.

10

15

20

25

30

-13-

1. A method for preparing a closed cell microcellular foam comprising the steps of:

(a) permeating a copolymer of at least one α-olefin and at least one α,β-monoethylenically unsaturated carboxylic acid, by pressurizing using an inert gas in the presence of a blowing agent and ammonia for an incubation time sufficient to effect a substantial diffusion of the inert gas, the blowing agent and the ammonia throughout the copolymer, the pressurizing being sufficient to maintain a pressure from about 1.4 mPag (200 psig) to about 20 mPag (3,000 psig); and thereafter

(b) heating the permeated copolymer in a field of electromagnetic radiation of from about 0.1 megahertz (MHz) to about 200 MHz to prepare a closed cell microcellular foam wherein the foam contains cells with a diameter of less than 10 μm.

2. A method as claimed in Claim 1, wherein the blowing agent is selected from chlorofluorocarbons and chlorofluorohydrocarbons.

3. A method as claimed in Claim 1 or Claim 2, wherein the pressure of step (a) is from about 1.4 mPag (200 psig) to about 5.5 mPag (800 psig).

4. A method as claimed in any one of the  
5 preceding claims, wherein the inert gas is nitrogen.

5. A method as claimed in any one of the  
preceding claims, wherein the field of electromagnetic  
radiation of step (b) is radiowave radiation with a  
10 frequency from about 6 MHz to about 100 MHz.

6. A method as claimed in any one of the  
preceding claims, wherein the copolymer comprises from  
about 70 weight percent to about 95 weight percent of an  
15  $\alpha$ -olefin and from about 5 weight percent to about 30  
weight percent of an  $\alpha,\beta$ -monoethylenically unsaturated  
carboxylic acid, based upon the weight of the copolymer.

7. A method as claimed in any one of the  
20 preceding claims, wherein the  $\alpha$ -olefin contains about 3  
to about 8 carbons and the  $\alpha,\beta$ -monoethylenically  
unsaturated carboxylic acid contains about 3 to about 8  
carbons.

25 8. A method as claimed in Claim 7, wherein  
the copolymer is poly(ethylene/acrylic acid).

9. A method as claimed in any one of the  
preceding claims, wherein the carboxylic acid is an  
30 ionomer.

10. A method as claimed in Claim 9, wherein  
the carboxylic acid is complexed with the cation of  
magnesium or lead.

-15-

11. A method as claimed in Claim 9 or Claim 10, further comprising the step of crosslinking of the copolymer of step (a).

12. A closed cell microcellular foam  
5 comprising a copolymer of at least one  $\alpha$ -olefin and at least one  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid wherein the foam has cells having diameters of less than 10  $\mu\text{m}$ .

10 13. A closed cell microcellular foam as claimed in Claim 12, wherein the copolymer is as defined in any one of Claims 6 to 11.

14. A closed cell microcellular foam as  
15 claimed in Claim 12 or Claim 13, wherein the cells have a diameter of about 2  $\mu\text{m}$  to about 5  $\mu\text{m}$ .

15. A closed cell microcellular foam as  
claimed in any one of Claims 12 to 14, wherein the  
20 density is from about 0.01 g/cm<sup>3</sup> (0.64 lb/ft<sup>3</sup>) to about 0.1 g/cm<sup>3</sup> (6.4 lb/ft<sup>3</sup>).

25

30

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/05866

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC  
IPC(5): C08J 9/04; 9/12; 9/14

U.S.CL. 264/51,53,D165; 521/82,94,98,149,910

## II. FIELDS SEARCHED

Classification System	Classification Symbols	Minimum Documentation Searched?
		Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched
U.S.	264/51,53,D165; 521/82,94,98,149,910	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of Document, <sup>1</sup> with indication, where appropriate, of the relevant passages <sup>2</sup>	Relevant to Claim No. <sup>3</sup>
X	US, A, 3,711,430 (RUBINS) 16 January 1973 Entire document	1-15
Y	US, A, 3,960,792 (NAKAMURA) 01 June 1976 Entire document	1-15
Y	US, A, 3,013,996 (POLLARD ET AL.) 19 December 1961 Entire document	1-15

<sup>1</sup> Special categories of cited documents: 10<sup>2</sup> "A" document defining the general state of the art which is not considered to be of particular relevance<sup>3</sup> "E" earlier document but published on or after the international filing date<sup>4</sup> "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<sup>5</sup> "O" document referring to an oral disclosure, use, exhibition or other means<sup>6</sup> "P" document published prior to the international filing date but later than the priority date claimed<sup>7</sup> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>8</sup> "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>9</sup> "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<sup>10</sup> "F" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

02 APRIL 1990

Date of Mailing of this International Search Report

18 APR 1990

International Searching Authority

ISA/US

Signature of Authorized Officer  
*Morton Foelak*  
 MORTON FOELAK